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PROCESS OF CEMENTATION

Harry K. Ihrig, Milwaukee, Wis., assignor to
Globe Steel Tubes Co., Milwaukee, Wis., a cor-
poration of Delaware

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This invention relates to a process of cementation of metals, particularly iron and steel, to render such metals non-corrosive and acid-resistant.

Cementation of metals with carbon and other elements is well known in the art. The use of phosphorus and certain phosphorus compounds such as phosphine is also old. Alloys of iron and phosphorus and copper-tin phosphorus bronzes are also old in the art. Prior methods for the introduction of phosphorus into metals by cementation, however, have employed either the element phosphorus alone, or volatile phosphorus compounds such as phosphine. Ordinary yellow phosphorus is a very dangerous substance to handle. It is very poisonous and spontaneously combustible in air and to preserve it it must be stored under water. Phosphine or hydrogen phosphide is likewise very poisonous and spontaneously inflammable. Furthermore, the cases formed in the base metal under these prior methods, while somewhat resistant to corrosive substances, are much less resistant than those of the process about to be described. The use of phosphorus in a coating metal, which in the case of copper and tin phosphide coatings gives a very acid resisting coating, has the disadvantage of being very brittle. Being a coating and not an integral part of the metal itself, it often cracks and spalls off, exposing the base metal to corrosion.

According to the present invention, phosphorus impregnation or cementation of the base metal is obtained with non-poisonous, non-inflammable, relatively inert, readily available, and inexpensive compounds of phosphorus, and the phosphorus is readily absorbed by the iron or steel to form a phosphorus case of appreciable depth, imparting to the resultant product highly desirable and advantageous characteristics such as superior and lasting corrosion-resisting properties. It is further contemplated according to the present invention to impregnate the iron or steel with copper either before, after, or during the impregnating of such metal with phosphorus to thus impart to the metal high acid-resisting properties in addition to the corrosion-resisting properties imparted thereto by the absorption of phosphorus.

I have discovered that when iron or steel articles are heated in contact with oxygen compounds of phosphorus such as phosphorus pentoxide, sodium metaphosphate or other relatively cheap phosphorus compounds such as certain fertilizer compounds, slags and ores, the iron reduces the oxide of phosphorus and the phosphorus formed in situ is readily absorbed by the iron to

form a phosphorus case. This reaction may be speeded up by the use of certain catalysts such as finely divided nickel. It may also be speeded up by an excess of iron. Thus, if an iron container is used, the reaction is catalyzed by the container.

The case produced by the absorption of phosphorus by the iron in this process, while resistant to atmospheric exposure and other mild corrosive agents, is not highly resistant to acids such as sulphuric acid. If, however, the case contains copper as well as phosphorus, it becomes highly resistant to sulphuric and other acids as well as to corrosion. The copper may be introduced simultaneously with the phosphorus or before or after the phosphorizing treatment. Any convenient method may be used, such as the treatment of the metal with copper chloride or with organic salts of copper at high temperatures as described and claimed, for instance, in my co-pending application Serial No. 732,305, filed June 25, 1934. In the simultaneous treatment, the copper salts may be mixed with the phosphorus compounds and then heated. Another method equally effective is to treat a copper steel with phosphorus compounds resulting in a case containing both phosphorus and copper.

As a laboratory example of the first method of cementation, a piece of low carbon seamless tube was packed in a larger steel tube closed at one end, with a mixture of 10 grams of phosphorus pentoxide, 10 grams of finely divided silica, and 3 grams of copper chloride. This was heated to a temperature between 1600° F. and 1900° F. in an electric furnace and maintained at such temperature for four hours with nitrogen gas running into the top of the container tube to replace the air. After cooling, the sample was found to have a copper colored surface and, on immersing a severed section of the tube in dilute sulphuric acid for twenty-four hours, the core was attacked by the acid while the case was resistant.

I have also discovered that in lieu of the chloride in the above example, in the use of which there is some danger of attack on the steel, the oxides of copper (either cuprous or cupric) may be used very effectively for impregnating the base metal with copper. The iron reduces the copper oxide at the high temperatures used and the copper in the nascent state is immediately absorbed by the base metal. This combination or use of two oxides—phosphorus and copper—to impregnate a base metal by cementation with the elements phosphorus and copper is believed to be entirely new in the art and to possess hereto-

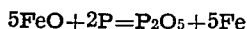
fore unrealized advantages in application, effectiveness and results obtained. Thus the following is an example of this modification of the first method above referred to as practiced in a pilot plant now in operation:

35 pounds of dry sand, 1 pound of phosphorus pentoxide and 1 ounce of cuprous oxide were placed in a substantially air-tight iron drum which was revolved slowly in a furnace. Two five-foot tubes were placed inside the drum with the above mixture. Nitrogen gas was introduced into one end of the drum and escaped through a water seal at the other end. The drum was started revolving and the furnace was brought up slowly to 1810° F. and held at this temperature for approximately four hours. It was then cooled down to room temperature and the tubes removed. They were found to have a smooth "gun metal" colored surface, and upon immersing a severed section of one of the tubes in dilute sulfuric acid for twenty-four hours, the core was attacked by the acid while the case was resistant.

As a laboratory example of the second method of cementation above referred to, a bar of low carbon 2% copper steel was packed in 3 grams of phosphorus pentoxide, 10 grams of finely divided silica, and 2 grams of nickel oxalate in a silica tube. This was heated for four hours at a temperature between 1600° F. and 1900° F. in an electric furnace with nitrogen gas passing through the container to replace the air. The sample after cooling showed a resistant case on being immersed in a 10% solution of sulfuric acid for twenty-four hours. The nickel oxalate included in this example functions as a catalyst and facilitates the reaction, permitting the same to occur at relatively lower temperatures when it is present in the mixture. Furthermore, it appears that the decomposition products of the nickel oxalate assist in the reduction of the phosphorus pentoxide.

In all the above examples, photomicrographs of the samples revealed substantial impregnation in the form of a case with the copper and phosphorus thoroughly and permanently penetrated into and combined and alloyed with the base metal of the piece. The result is a true cementation and not a mere coating. Crushing the impregnated tube shows the case to be very ductile and no spalling of the case takes place even under extreme distortion. The alloy produced by my process may be termed a cementation alloy as distinguished from an alloy produced by fusion.

One purpose of the finely divided silica in the mixture is to dilute the phosphorus compounds, but it is believed that the presence of the silica also aids in the reaction by facilitating the reduction of the P_2O_5 . The equilibrium may be expressed as follows:



The silica and the catalyst may be used over and over by enrichment at the beginning of each run with the phosphorus compounds.

One identifying characteristic of the invention is the production of a phosphorus case in iron or steel by the heating of such metal in contact with oxygen compounds of phosphorus into which case, if desired, copper may also be introduced by copperizing a non-copper steel before, after, or simultaneously with, the phosphorizing process. The same result may be attained by phosphorizing a copper steel. The process and the resultant article are believed to be new

in the art and to represent a decided advance therein. The use of free phosphorus and the dangerous compounds of phosphorus heretofore employed is avoided. The penetration is positive and substantial and the case is more ductile and acid and corrosion-resistant than those produced according to prior practices.

In practicing the invention, other or additional inert or reducing agents may be employed such as carbon, hydrogen or city gas. I have found that by the use of finely divided carbon, the reaction can be made to take place at lower temperatures and that carburizing does not occur if an atmosphere of nitrogen is employed. I have also found that by the use of city gas instead of nitrogen as an atmosphere, a phosphide case is obtained, but carbon is also absorbed. By mixing nitrogen with city gas, the carburizing action is cut down, while the reducing action of the city gas speeds up the phosphorizing reaction, especially at lower temperatures.

I claim:

1. The process of impregnating with phosphorus by cementation a metal capable of alloying with phosphorus which consists in heating the metal under non-oxidizing conditions in contact with an oxygen compound of phosphorus, at temperatures sufficient to decompose said phosphorus compound.

2. The process of impregnating with phosphorus and copper by cementation a metal capable of alloying with phosphorus and copper which consists in heating the metal under non-oxidizing conditions in contact with an oxygen compound of phosphorus and a copper salt at temperatures sufficient to decompose said phosphorus and copper compounds.

3. The process of impregnating with phosphorus and copper by cementation a metal capable of alloying with phosphorus and copper which consists in heating the metal under non-oxidizing conditions in contact with an oxygen compound of phosphorus at a temperature sufficient to decompose the phosphorus compound, and thereafter heating the metal under the same conditions in contact with a copper salt at temperatures sufficient to decompose said copper salt.

4. The process of impregnating with phosphorus and copper by cementation a metal capable of alloying with phosphorus and copper which consists in heating the metal under non-oxidizing conditions in contact with an oxygen compound of phosphorus at a temperature sufficient to decompose the phosphorus compound, and thereafter or prior thereto or simultaneously therewith heating said metal under the same conditions in contact with a copper salt at a temperature sufficient to decompose the copper salt.

5. The process of impregnating copper steel with phosphorus by cementation which consists in heating the copper steel under non-oxidizing conditions in contact with an oxygen compound of phosphorus at temperatures sufficient to decompose the phosphorus compound.

6. The process of impregnating iron or steel with phosphorus and copper by cementation which consists in heating said metal under non-oxidizing conditions in contact with a mixture of phosphorus pentoxide, silica, and a salt of copper at temperatures sufficient to decompose the phosphorus and copper compound.

7. The process of impregnating iron or steel

with phosphorus and copper by cementation which consists in heating the metal under non-oxidizing conditions in contact with an oxygen compound of phosphorus, a salt of copper, and a catalyst at temperatures sufficient to decompose the compounds of phosphorus and copper.

8. The process of impregnating iron or steel with phosphorus by cementation which consists in heating the metal under non-oxidizing conditions in contact with an oxygen compound of phosphorus and a catalyst at a temperature sufficient to decompose the phosphorus compound.

9. The process of impregnating iron or steel with phosphorus by cementation which consists in heating the metal under non-oxidizing conditions in contact with phosphorus pentoxide at a temperature sufficient to decompose the phosphorus pentoxide.

10. The process of impregnating with phosphorus and copper by cementation a metal capable of alloying with phosphorus and copper which consists in heating the metal under non-oxidizing conditions in contact with an oxygen compound of phosphorus and an organic salt of copper at temperatures sufficient to decompose the compounds of phosphorus and copper.

11. The process of impregnating with phosphorus and copper by cementation a metal capable of alloying with phosphorus and copper which consists in heating the metal under non-oxidizing conditions in contact with a copper salt at a temperature sufficient to decompose the copper salt, and thereafter heating the metal under the same conditions in contact with an oxygen compound of phosphorus at a temperature sufficient to decompose the phosphorus compound.

12. A cementation compound for the treatment of iron or steel to provide the latter with a non-oxidizing and corrosion-resisting case, consisting of an oxygen compound of phosphorus, and a catalyst.

13. A cementation compound for the treatment of iron or steel to provide the latter with a non-oxidizing, corrosion- and acid-resisting cementation case, consisting of an organic salt of copper, and an oxygen compound of phosphorus.

14. A cementation compound for the treatment of iron or steel to provide the latter with a non-oxidizing, corrosion- and acid-resisting cementation case, consisting of an organic salt of copper, an oxygen compound of phosphorus, finely divided silica, and a catalyst.

15. The process of impregnating iron or steel with phosphorus and copper by cementation which consists in heating the metal under non-oxidizing conditions in contact with an oxygen compound of phosphorus, finely divided silica, and a copper salt in an iron container at temperatures sufficient to decompose the phosphorus and copper compounds.

16. The process of impregnating iron or steel with phosphorus and copper by cementation which consists in heating the metal under non-oxidizing conditions in contact with an oxygen compound of phosphorus, finely divided silica, and nickel oxalate in a closed container at temperatures sufficient to decompose the phosphorus compound.

17. The process of impregnating iron or steel with phosphorus by cementation which consists in heating the metal under non-oxidizing conditions in contact with an oxygen compound of phosphorus and finely divided nickel at a tem-

perature sufficient to decompose the phosphorus compound.

18. The process of impregnating iron or steel with phosphorus by cementation which consists in heating the metal under non-oxidizing conditions in contact with an oxygen compound of phosphorus in an iron container at a temperature sufficient to decompose the phosphorus compound.

19. The process of impregnating iron or steel with phosphorus by cementation which consists in heating the metal under non-oxidizing conditions in contact with an oxygen compound of phosphorus and silica at a temperature sufficient to decompose the phosphorus compound.

20. The process of impregnating with phosphorus by cementation a metal capable of alloying with phosphorus which consists in heating the metal in contact with an oxygen compound of phosphorus, and finely divided carbon in a nitrogen atmosphere at a temperature sufficient to decompose the phosphorus compound.

21. The process of impregnating with phosphorus by cementation a metal capable of alloying with phosphorus which consists in heating the metal in contact with an oxygen compound of phosphorus in an atmosphere of city gas at a temperature sufficient to decompose the phosphorus compound.

22. The process of impregnating with phosphorus by cementation a metal capable of alloying with phosphorus which consists in heating the metal in contact with an oxygen compound of phosphorus in an atmosphere of city gas and nitrogen at a temperature sufficient to decompose the phosphorus compound.

23. The process of impregnating iron or steel with phosphorus and copper by cementation which consists in heating the metal under non-oxidizing conditions in contact with oxides of phosphorus and copper at temperatures sufficient to decompose the oxides of phosphorus and copper.

24. The process of impregnating iron or steel with phosphorus and copper by cementation which consists in heating the metal under non-oxidizing conditions in contact with oxides of phosphorus and copper at temperatures sufficient to decompose the oxides of phosphorus and copper, and in the presence of a catalyst.

25. A cementation compound for the treatment of iron or steel to provide the latter with a non-oxidizing, corrosion and acid resisting cementation case consisting of an oxygen compound of phosphorus, silica, and an oxide of copper.

26. As a new article of manufacture, iron or steel having a cementation case containing phosphorus and copper made in accordance with the process described in claim 2.

27. As a new article of manufacture, iron or steel having a cementation case containing phosphorus and copper made in accordance with the process described in claim 4.

28. As a new article of manufacture, iron or steel having a copper iron core and a copper phosphorus iron cementation case made in accordance with the process described in claim 5.

29. As a new article of manufacture, a copper bearing steel having a cementation case containing phosphorus or a compound of phosphorus made in accordance with the process described in claim 5.

HARRY K. IHRIG.